



Methanothermal treatment of carbonated mixtures of PbSO_4 and PbO_2 to synthesize α - PbO for lead acid batteries



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HIGHLIGHTS

- PbO can be prepared by a solvothermal reaction of mixture of PbSO_4 and PbO_2 within methanol.
- The prepared PbO can discharge a capacity of 170 mAh g^{-1} at 5 mA g^{-1} .
- The prepared PbO has the discharge capacity of 80 mAh g^{-1} at 200 mA g^{-1} .
- This paper shows a new way for the recycle of spent lead acid battery.

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ABSTRACT

We have developed a novel route to make new batteries from spent ones, in which we obtain and regenerate the active materials of positive electrode and negative electrode respectively. For the spent lead acid batteries, the positive electrode active materials contain both PbSO_4 and PbO_2 . To make full use of them, we have to investigate the treatment of the mixtures rather than only PbO_2 , which we have reported previously. Here we report our investigation on three mixtures of PbSO_4 and PbO_2 in different mole ratios, as well as the electrode materials directly from the spent batteries. The mixtures are firstly desulphated, and then solvothermally processed in methanol at 140°C for 24 h. The as-obtained solids contain both $\text{PbO} \cdot \text{PbCO}_3$ and PbCO_3 , which have been calcined to form α - PbO . The α - PbO powders are similar irregular particles and highly electrochemically active, which discharge around 170 mAh g^{-1} at 5 mA g^{-1} , 80 mAh g^{-1} at 200 mA g^{-1} and 60 mAh g^{-1} at 400 mA g^{-1} with excellent cyclic stability in 50 cycles.

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1. Introduction

Due to growing energy requirements, the world's attention is focused on sustainable and renewable energy, especially all forms of solar energy [1–3]. Solar energies incorrigible depend on the weather, which has to be stabilized by energy storage systems for normal uses [4–6]. Although great progresses have been made in Li-ion battery techniques [7–9], lead-acid batteries are still the most widely used energy storage batteries because of their low-cost, reliability and safety [10–13]. This has produced huge amounts of spent batteries and requires effective recycling techniques.

Usually, lead paste obtained from the separation of spent lead acid batteries is composed of PbSO_4 , PbO_2 , PbO and lead metal/alloys. This complexity leads to many difficulties in the subsequent

processes [14,15]. Currently, lead paste is reduced to metallic lead through a pyrometallurgical process (please refer to the current process in Fig. 1), however, due to its requirement of high temperature (around 1000°C), the traditional pyrometallurgical process requires huge amounts of energy and causes risks of pollution. For example, SO_2 and lead dust will generate in some processes without fully desulphation, especially in some underdeveloped areas. Thus, more and more attentions are paid to the green recycling process for spent lead acid batteries, such as hydrometallurgical routes [16,17].

We have developed a novel route from 2009 [18–20] to produce new batteries from the spent ones based on fully separation of battery components (please refer to the new process in Fig. 1) and subsequent respective production of new positive and negative active materials through chemical treatment of them at temperature lower than 500°C . Recently, we have demonstrated that calcination of the product of PbO_2 treated in methanol under solvothermal conditions can produce highly electrochemically active

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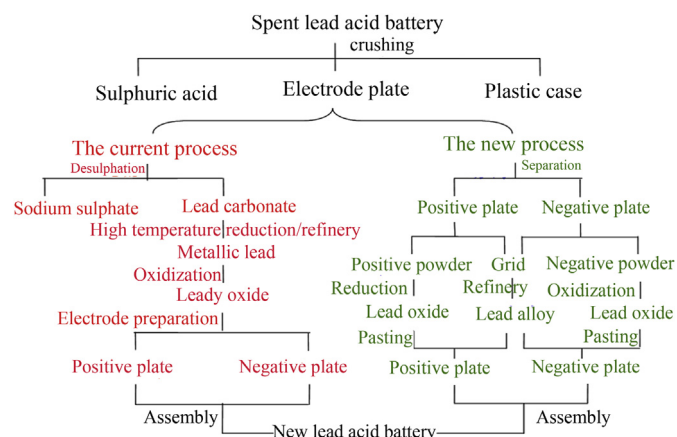


Fig. 1. The novel route of the recycle of the lead acid battery in comparison with the current one. After the separation of sulphuric acid, electrode plates and plastic case, the current route reduces the leady mixture to metallic lead. After purification, this lead is used to produce the leady oxide for production of lead acid batteries; the new route suggested by us does further separation of positive electrode from negative electrode, and again further separation of the active materials from the grid for the both electrodes. Only then, the active materials are chemically treated to obtain the regenerated active materials for production of new batteries. Obviously, new route employs more physical separations to avoid over-chemical-treatments and subsequent pollution risks.

α -PbO that can discharge 120 mAh g^{-1} at 50 mA g^{-1} in positive electrode with excellent cycle stability [21]. However, the positive electrode materials from the spent batteries consist of both PbSO_4 and PbO_2 . We have been wondering if the same process still works for the mixture, because PbSO_4 or PbCO_3 (formed after desulphation of PbSO_4 with a carbonate) may interfere with the reaction even if either of them does not react with methanol under solvothermal conditions.

Therefore, we have investigated the treatments of three mixtures of PbSO_4 and PbO_2 as well as the actual materials from the spent positive material to get α -PbO for new lead acid battery, which we have found the treatment is as effective as aforementioned PbO_2 -only case.

2. Experimental

2.1. Material preparation

Firstly, three fine mechanical mixtures of lead sulphate (AR grade, 99.0%, Aladdin Chemical Reagent Co., Ltd.) and lead dioxide (AR grade, 98.0%, Aladdin Chemical Reagent Co., Ltd.) at different molar ratios of 2:1, 1:1 and 1:2 were prepared. Also, the positive electrode materials are obtained from the positive electrode of spent batteries.

The desulphation of each of the mixtures was carried out as follows: 2.0 g of the mixture was added to a three-necked flask with 100 mL of 0.1 mol L^{-1} ammonium carbonate solution inside. The suspension was stirred at 30°C for 2 h. The solid obtained was then filtered and dried at 100°C .

The solvothermal treatment of the desulphated mixture was carried out as follows: 20 mL of methanol (99.5%, Sinopharm Chemical Reagent Co., Ltd.) and the desulphated mixture was added to a Teflon-lined stainless steel autoclave, which was heated at 140°C under stirring for 24 h. The solid was then separated and dried for the next use.

To prepare α -PbO for the electrochemical studies, the solid obtained from the solvothermal process was calcined at 450°C for one hour in a muffle furnace. The cooled samples was then added into ethanol to ultrasonicate for 30 min, and then filtered and dried.

The as-prepared α -PbO samples prepared from the mixtures of PbSO_4 and PbO_2 in the molar ratios of 2:1, 1:1 and 1:2 will be denoted as A, B and C sequentially. The one from the spent positive materials will be denoted as the spent.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns of the samples were measured on a Bruker D8 Discover instrument operating at 40 kV and 20 mA, by using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$), and their phase compositions were determined by the software Jade. Scanning electron micrographs (SEM) of samples were taken on a Hitachi S-4800 microscope.

2.3. Electrode preparation

1.0 g of each of the as-prepared samples (A, B, C or the spent) was placed in a container, and then 0.003 g of fibres, 0.003 g of graphite, 0.124 mL of water and 0.11 mL of H_2SO_4 (36 wt.%) were slowly added to it under grinding. The amount of water added could be slightly modified to obtain the required density (4.0 g mL^{-1}). The obtained paste was put evenly onto a Pb–Ca alloy grid with dimensions of $10 \times 8 \times 2 \text{ mm}^3$, which was then pressed to form a positive plate.

The plate was immersed in a sulphuric acid of 8 wt.% for 5 s, and then put into an oven maintained at 100°C for 5 min, then put above a water bath maintained at 75°C . The curing process was maintained for 24 h. After that, the plate was dried at 70°C for 48 h. The mass of the active material is the mass difference of the dried plate subtracts the blank grid used.

2.4. Electrochemical performance test

All the formation and the cycling tests were carried out with an NEWARE Cycler (BTS-5V3A Shenzhen NEWARE Electronics Co., Ltd., China). The positive plate was assembled with a commercial negative plate (from commercial batteries, the area is about 3 times of the positive plate) which are separated by absorptive glass-mat (AGM). The electrodes were assembled into a case and the electrolyte was H_2SO_4 solution with a relative density of 1.23 g mL^{-1} .

After the plate had been soaked for 2 h, the battery formation was started. The formation was divided into 3 steps. Firstly, the electrode was charged at a current density of 15 mA cm^{-2} to 100 mAh g^{-1} ; then it is charged at 25 mA cm^{-2} for another 150 mAh g^{-1} ; and finally, it was charged at 8 mA cm^{-2} for another 100 mAh g^{-1} . Since the negative electrode had a much larger capacity than the positive electrode, the cell capacity was restricted by the positive electrode.

After the battery formation, the cell was discharged at 5 mA g^{-1} until the voltage fell to 1.75 V. Then it was used for cyclic tests. The electrode was firstly charged at 50 mA g^{-1} until the cell voltage reached to 2.45 V, then it was charged at 25 mA g^{-1} until the charged charges was 110% of the first discharge capacity after the formation. The electrode was then discharged at a current density of 50 mA g^{-1} . This was done for 50 cycles. Different discharge current density tests were done after 50 cycles except the one at 5 mA g^{-1} , these data (discharge at 5 mA g^{-1}) were obtained at the first discharge capacity after the formation.

The cyclic voltammetry (CV) is carried out on the CorrTest model CS350 electrochemical working station (WUHAN CORRTEST Instrument Co., Ltd., China). The CV curves were determined with a typical three-electrode system. The working electrode was prepared with a plate filled with lead monoxide, and a double platinum electrode was used as the counter electrode while the $\text{Hg/Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$ (sat.) was employed as the reference electrode.

Sulphuric acid (36 wt.%) was used as electrolyte. The measurement was carried out at a potential scan rate of 20 mV s^{-1} from 0 to 1.8 V.

3. Results and discussion

3.1. Treatments of the mixtures of PbSO_4 and PbO_2

Fig. 2 shows the schematic flow sheet of the treatments of the mixtures of PbSO_4 and PbO_2 . It is divided into three steps: desulphation, solvothermal reaction and calcination.

3.1.1. Desulphation of mixtures of PbSO_4 and PbO_2

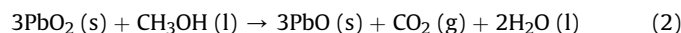
Fig. 3 shows the XRD patterns of mixtures of PbSO_4 and PbO_2 before and after desulphation. Both PbSO_4 and PbO_2 are found for sure before the desulphation (Fig. 3a, b and c), and the relative intensities of diffraction peaks corresponding to PbO_2 increase according to the increase of its content. After the desulphation, PbCO_3 appears instead of PbSO_4 (Fig. 3d, e and f), but PbO_2 is still there. Therefore, PbSO_4 has been converted into PbCO_3 (Eq. (1)):



It is known that the solubility constants of PbCO_3 and PbSO_4 are 3.3×10^{-14} and 1.06×10^{-8} , respectively. Thus, the equilibrium constant of Eq. (1) is 3.2×10^5 , which means PbSO_4 can be transformed into PbCO_3 completely. We have made sure that the desulphation is completed by chemical tests, therefore, the yields for desulphation should be 100%.

3.1.2. The solvothermal reaction of mixtures in methanol

The XRD patterns of the samples after solvothermal reaction were respectively shown in Fig. 4. As we have reported before, that PbO_2 is reduced to PbO (Eq. (2)) at 140°C for 24 h through solvothermal treatment in methanol of desulphated solids, which are composed of PbO_2 and PbCO_3 [21].



However, because there is already PbCO_3 before reduction, the produced PbO reacts with PbCO_3 to produce $\text{PbO} \cdot \text{PbCO}_3$ (Eq. (3)):



There is one big difference from the result in our previous research, where no PbCO_3 exists in the starting materials [21]. Also, the more lead sulphate in the original mixture is, the more lead carbonate in the sample is.

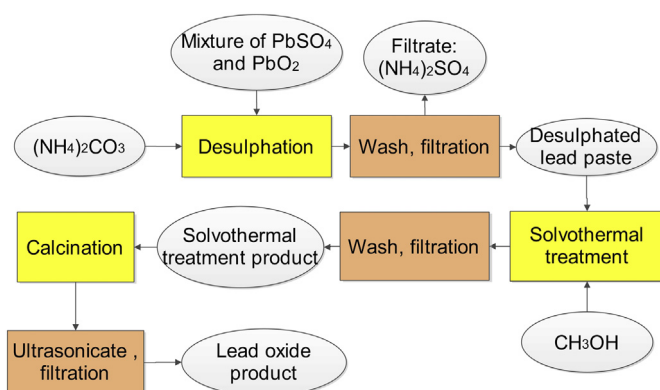


Fig. 2. Schematic flow sheet of the novel process for mixtures of PbO_2 and PbSO_4 .

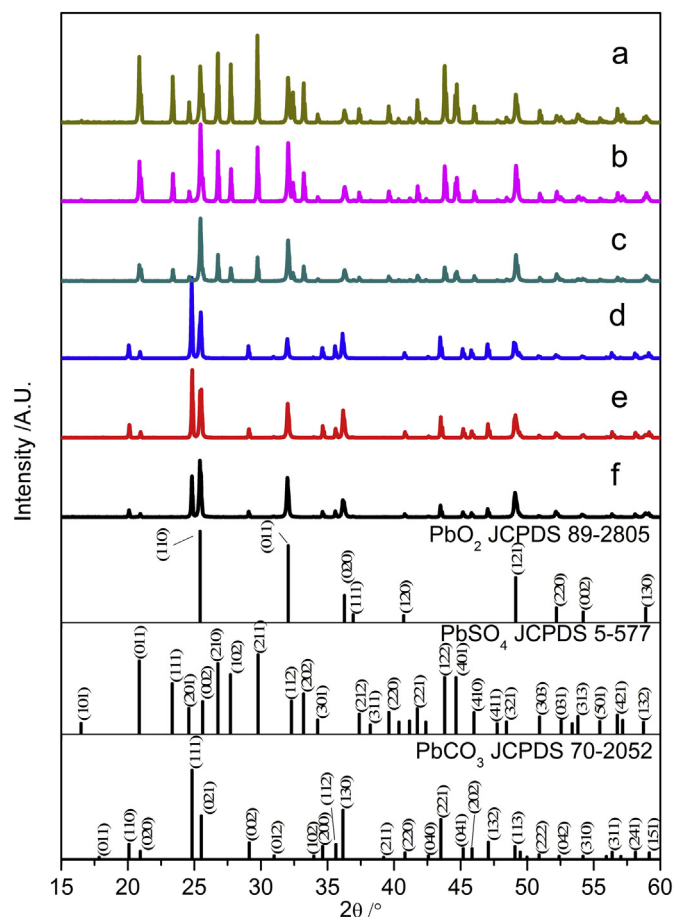


Fig. 3. XRD patterns of the samples before (a, b, c) and after (d, e, f) desulphation. The mole ratios of lead sulphate and lead dioxide in samples were 2:1 (a, d), 1:1 (b, e) and 1:2 (c, f).

3.1.3. The calcination of the mixtures after solvothermal treatments

Fig. 5 shows the XRD patterns of mixtures obtained from the solvothermal products being calcined at 450°C for one hour, which shows that there are both α - PbO and Pb_3O_4 in the samples. It has been known that PbCO_3 decomposes in three steps between 180 and 350°C (Eqs. (4)–(6)) [21,22], therefore, decomposition of

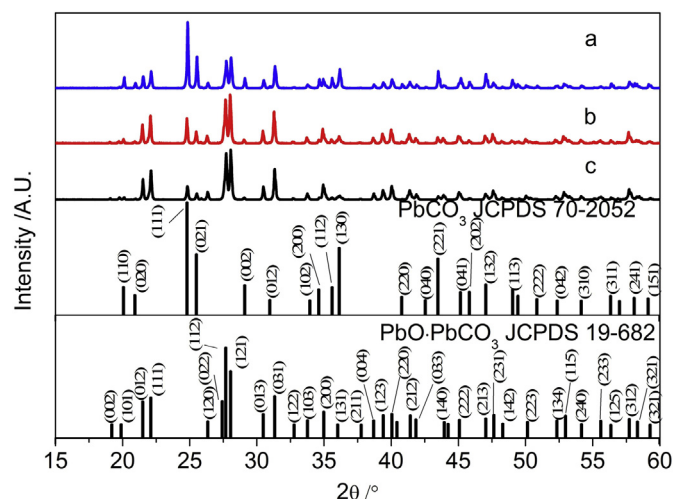


Fig. 4. XRD patterns of the samples after solvothermal reaction. The mole ratios of lead sulphate and lead dioxide in samples were 2:1 (a), 1:1 (b) and 1:2 (c).

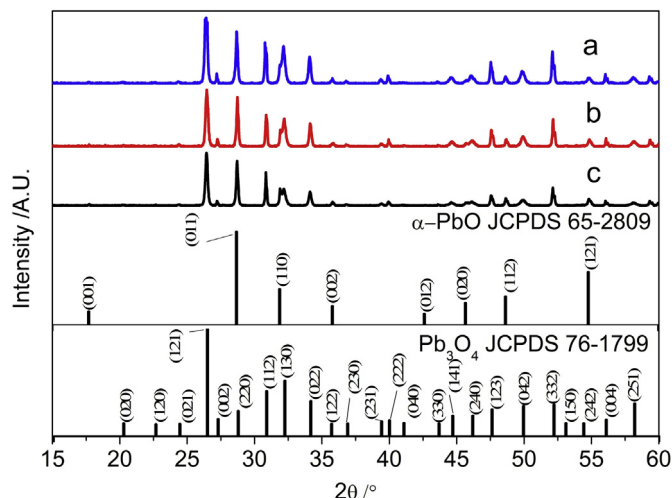


Fig. 5. XRD patterns of the solvothermal samples after calcination at 450 °C for one hour. The mole ratios of lead sulphate and lead dioxide in the original mixtures were 2:1 (a), 1:1 (b) and 1:2 (c).

PbCO₃, together with the existed PbO·PbCO₃ produces α-PbO at 450 °C. Here, part of PbO has been oxidized by O₂ in air to form Pb₃O₄ as reported. According to the phase composition analyses supplied by the Program Jade, the composition of the final mixtures are calculated and shown in Table 1, which shows that all three samples are similar in composition and about a quarter of the final products are Pb₃O₄. Therefore, the original composition of the PbSO₄ and PbO₂ has little influence in the final product, but it may be sensitive to the conditions in furnace:

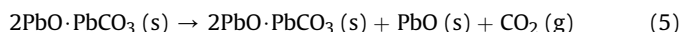
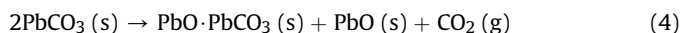


Fig. 6 shows the SEM micrographs of the three calcined samples A, B and C. It shows that all the three samples are similar irregular particles, of which the longest dimension is mostly less than 2 μm.

We believe that only the as-formed PbCO₃ from desulphation could affect the crystallization/precipitation of PbO or PbCO₃ from the reduction of PbO₂. By studying three artificial mixtures of PbSO₄ and PbO₂, we found that the compositions of the mixture have little effect on the property of the final products. Therefore, we decided not to do the time and money exhausting measurements on the intermediates. For the final products after solvothermal reactions, we have done all necessary analyses. The XRD patterns show no existence of PbO₂, therefore, the reaction should be almost 100% completion.

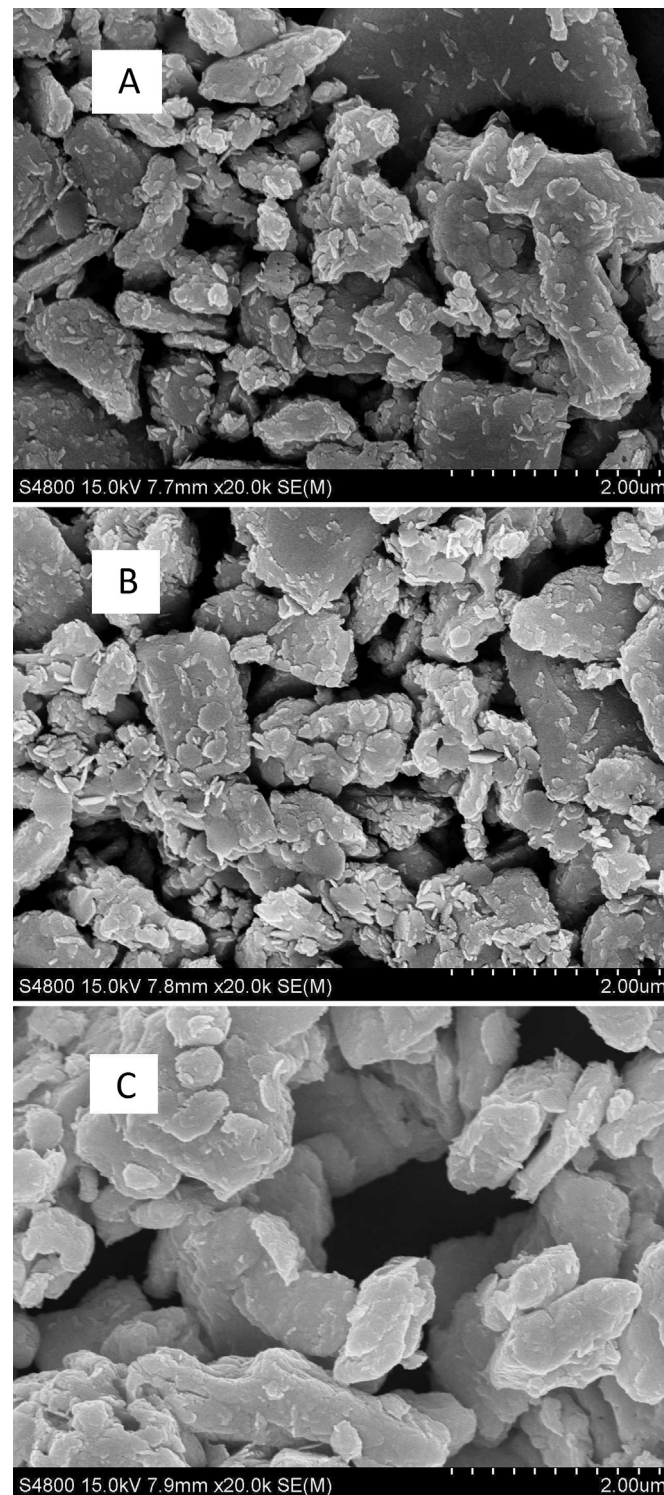


Fig. 6. SEM micrographs of the solvothermal reaction samples after calcination at 450 °C for one hour. The mole ratios of lead sulphate and lead dioxide in the starting mixtures are (A) 2:1, (B) 1:1 and (C) 1:2.

3.2. The product after the formation in positive electrode of a lead acid battery

Fig. 7 shows the XRD patterns of the three samples obtained after formation of samples A, B and C in the positive electrodes, which tells that all the three samples contain β-PbO₂ and PbSO₄. By

Table 1

The composition of the samples A, B and C after calcination.

Sample	Composition (wt.%) ^a	
	α-PbO	Pb ₃ O ₄
A	73.6	26.4
B	72.6	27.4
C	73.4	26.6

^a The compositions were determined according to the XRD patterns shown in Fig. 5 with the software Jade.

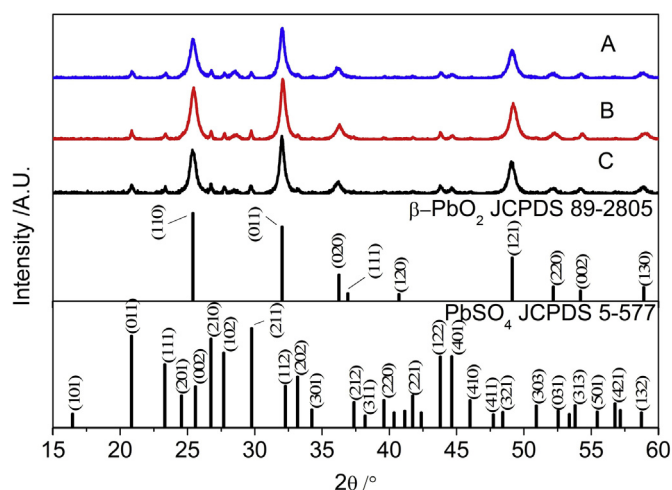


Fig. 7. XRD patterns of the samples after formation. The mole ratios of lead sulphate and lead dioxide in samples were (A) 2:1, (B) 1:1 and (C) 1:2.

using the Program Jade, the contents of PbO_2 are calculated and listed in Table 2. Combined with Table 1 and Fig. 5, it could be concluded that higher amounts of Pb_3O_4 may produce more $\beta\text{-PbO}_2$. This is in accordance with the general knowledge on this particular issue [23–25].

To observe the morphology changes of the sample during the formation, the active materials were peeled from the electrode after formation, and then grinded for SEM observations (Fig. 8). It can be seen that the particles become much smaller after formation, and they are rod-like now with a diameter of 50 nm and a length of 200 nm. Therefore, large irregular particles of PbO transform into much smaller rod-like particles of PbSO_4 during the formation, and there are complete changes both in chemical structures and morphology. Again, there are little differences between the three samples.

3.3. Electrochemical performance of the prepared samples

Fig. 9 shows cyclic performance of the three samples, in which the discharge current density is all 50 mA g^{-1} . It can be seen that the discharge capacities of the three samples are all about $120\text{--}130 \text{ mAh g}^{-1}$, and quite stable within 50 cycles. Their capacity losses relative to the highest discharge capacity are less than 5% in 50 cycles when they are fully charged and discharged. The highest discharge capacities are 125, 131 and 126 mAh g^{-1} , corresponding to starting mole ratios of 2:1, 1:1 and 1:2 for lead sulphate and lead dioxide. Taking the test error of experiments into account, we can see that three samples have the very close discharge capacities. This is in accordance with the similar compositions at different stage of the treatments. Therefore, the mole ratios of lead sulphate and lead dioxide in the original mixture have little effect on the electrochemical performance, but difference in the content of Pb_3O_4 formed during calcination may have a stronger influence.

In comparison with the electrochemical performance of the product obtained from solvothermal treatment of the pure PbO_2 in methanol, we find that the initial discharge capacities of the

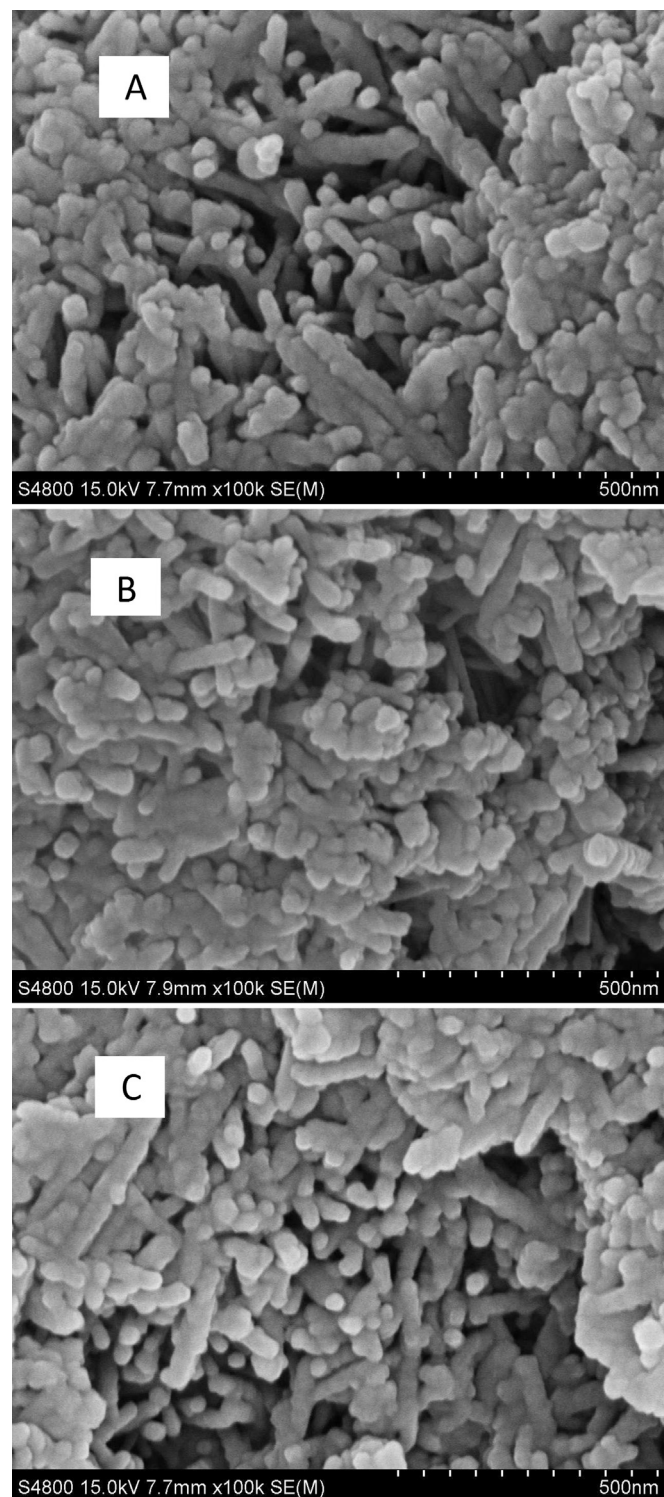


Fig. 8. SEM micrographs of the samples after formation. The mole ratios of lead sulphate and lead dioxide in samples were (A) 2:1, (B) 1:1 and (C) 1:2.

Table 2
The contents of PbO_2 after formation determined by the Jade software.

Sample	Contents of $\beta\text{-PbO}_2$ (wt.%)
A	94.4
B	95.6
C	94.7

products of the mixtures are as good, but the capacity loss is increased from 1% to 5% after 50 cycles. That may be due to the different particle sizes, because the particle sizes of the samples from the mixtures are a little bigger than the one from pure PbO_2 .

Fig. 10 shows the curve of discharge capacity versus the discharge current density. As expected, the discharge capacity decreases as the current density increases. The discharge performances of all the

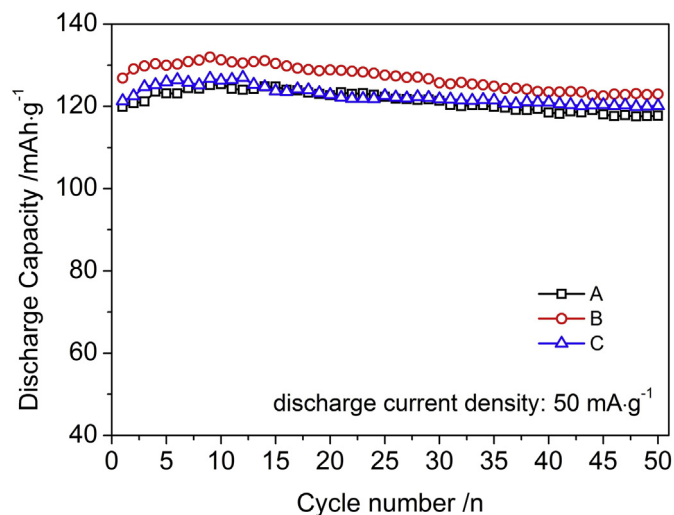


Fig. 9. Discharge capacity versus cycle number of the three samples. The mole ratios of lead sulphate and lead dioxide in samples were (A) 2:1, (B) 1:1 and (C) 1:2.

three samples are very similar, which discharge about 170 mAh g^{-1} at the current density of 5 mA g^{-1} , 80 mAh g^{-1} at 200 mA g^{-1} , and 60 mAh g^{-1} at 400 mA g^{-1} [21]. And the material utilizations of all the three samples at different mole ratios are about 70.3%, 70.9% and 69.8%, and they are also similar to our previous report.

The calcined products were also examined by cyclic voltammetry, which give the similar results to those of Visscher [26]. Fig. 11 shows CV curves of the three samples after the 50th cycle. It can be seen that the oxidation of PbSO_4 to PbO_2 occurs at 1.25 V (vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$ in sat. K_2SO_4), the evolution of oxygen occurs beyond 1.4 V, and the reduction of PbO_2 to PbSO_4 is at 0.93 V. All the CV curves are similar, and the cathode current is much higher than the anode current.

3.4. The treatments and the electrochemical performance of the positive material from spent lead acid battery

Fig. 12 gives the electrochemical performance of the material obtained from the spent positive material after the same

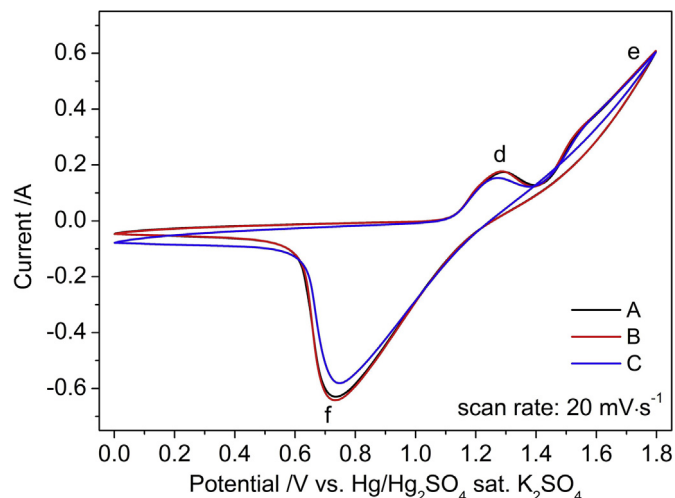


Fig. 11. Cyclic voltammetry curves of the three samples. The mole ratios of lead sulphate and lead dioxide in samples were (A) 2:1, (B) 1:1 and (C) 1:2.

treatments as the mechanical mixtures. Cyclic performance of the spent sample is shown in Fig. 12a, which shows that the capacity is around 120 mAh g^{-1} within the 50 cycles. Its capacity loss is about 10% within 50 cycles under 100% DOD. Fig. 12b shows the curve of discharge capacity versus the discharge current density. The discharge capacities are 160 mAh g^{-1} at the current density of 5 mA g^{-1} , and 40 mAh g^{-1} at 400 mA g^{-1} . The material utilization of the spent sample is about 67%. In comparison with the as-prepared samples from the mixtures, we find that the discharge capacity of the spent sample is 120 mAh g^{-1} , a little lower than those of the mixtures. Especially, the capacity loss of the reused sample is 10%, which is much bigger than those from the mixtures. This difference may be attributed to the impurities (such as additives, metal impurities) contained in the spent positive materials. We conjecture that the lower capacity of the spent positive material may due to the presence of additives, because they may not be active material but increases the mass of the active material, therefore, we will do more researches (such as component analysis and element content analysis) to figure out the mechanism.

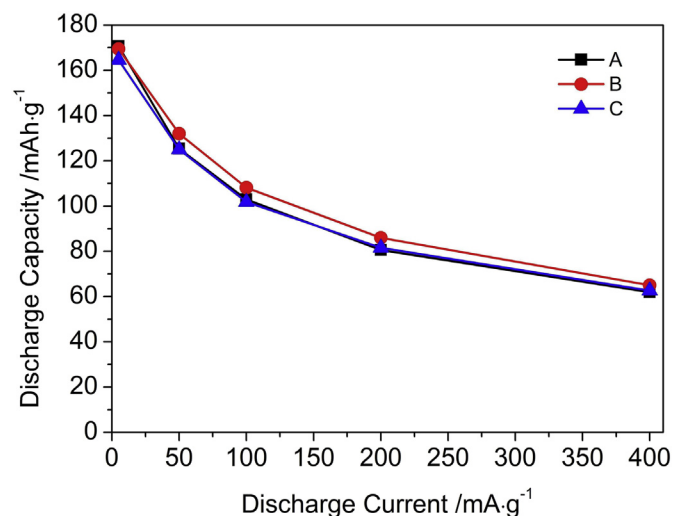


Fig. 10. Discharge capacity versus the current density of the three samples. The mole ratios of lead sulphate and lead dioxide in samples were (A) 2:1, (B) 1:1 and (C) 1:2.

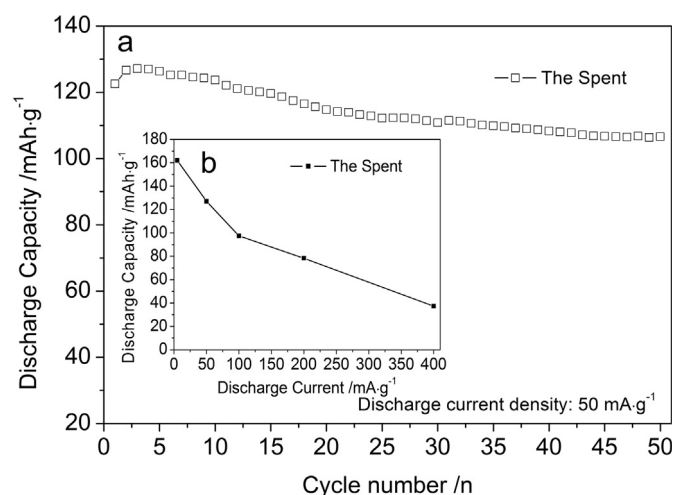


Fig. 12. Electrochemical performance of the spent positive material after treatments: (a) discharge capacity versus cycle number, (b) discharge capacity versus the current density.

4. Conclusion

Three mixtures of PbSO_4 and PbO_2 have been desulphated and then solvothermally treated to form $\alpha\text{-PbO}$ for lead acid batteries. The results show that PbSO_4 in the mixtures is easily transformed into PbCO_3 during desulphation process. Furthermore, all the desulphated mixtures are converted to $\text{PbO} \cdot \text{PbCO}_3$ or PbCO_3 during solvothermal treatments at 140°C for 24 h in methanol.

Calcination of all the solvothermal products at 450°C for one hour can produce mixtures of $\alpha\text{-PbO}$ and Pb_3O_4 . The compositions of the mixtures are very similar, in spite that the original compositions of the starting mixtures are very different. The SEM images show that all the products are similar irregular particles with longest dimension mostly less than $2\text{ }\mu\text{m}$.

Electrochemical performances of the three samples also show no great difference in discharge capacities, which are about 170 mAh g^{-1} at 5 mA g^{-1} , and 60 mAh g^{-1} at 400 mA g^{-1} . Moreover, all the as-prepared samples behave excellently in cyclic stability during 50 cycles.

The same treatments have been done to a sample from spent positive material. The results show that the capacity is all around 120 mAh g^{-1} within 50 cycles, and its capacity loss is about 10% in 50 cycles. In comparison with the samples prepared from the mixtures, we find that the discharge capacity of the spent sample is a little lower and capacity loss is also bigger. This difference may be attributed to the impurities in the original spent positive material, which has to be identified in the future work.

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